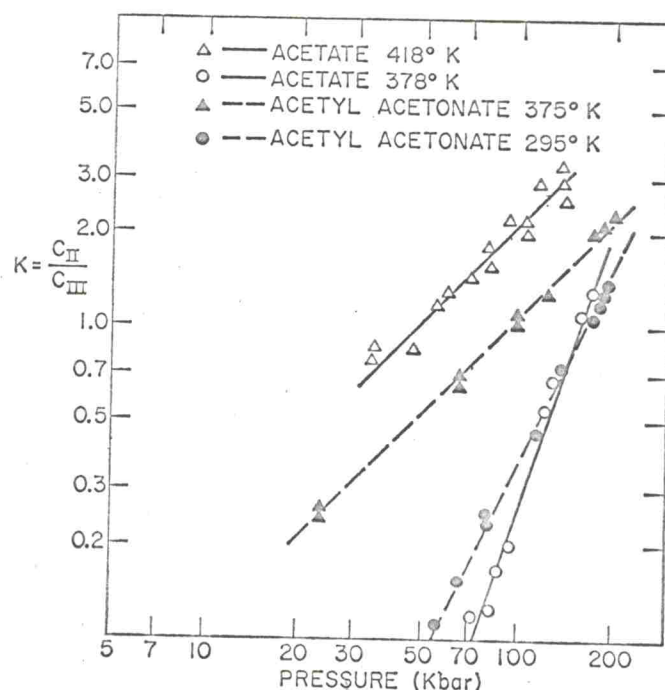Fig. 2. ln K vs. ln P—Ferric halides

Fig. 3. ln K vs. ln P—Acetylacetonate and basic acetate.

much over 90% are difficult to establish accurately, so one cannot say whether this description is applicable at very high dilution. For the halides, as well as for several other compounds which can be classified as relatively ionic, $B \cong 0.5$ with little temperature dependence. This corresponds to values of $\Delta\overline{V}$ which range from about 1.2 cc at 10 kilobars to about 0.06 cc at 200

kilobars. As discussed later, the conversion introduces stresses in the neighborhood of the reduced site. One can insert a term of the form

$$-\Sigma \varepsilon_i d\sigma_i$$

in the free energy, where ε and σ refer to strains and stresses introduced by the reduction. Then the ΔV of Eq. 2 can be written:

$$\Delta\overline{V} = \Delta V' - \sum_i \varepsilon_i \frac{\partial \sigma_i}{\partial p} \qquad (4a)$$

or, in the language of solution theory:

$$\Delta\overline{V} = \Delta V' - \frac{\partial V_e}{\partial C_{II}} \qquad (4b)$$

where $\Delta V'$ is the difference in unstrained volumes of the ferric and the ferrous site, and V_e is the excess volume of mixing. Since V_e is strongly concentration dependent, and the concentration of ferrous sites varies with pressure as discussed above, one can understand why ΔV varies with pressure. It can be shown that a small value of B implies a large negative value of

$$\frac{\partial V_e}{\partial C_{II}}$$

at low concentration of ferrous sites (low pressure), and strong coupling between adjacent sites, whereas large B implies weak coupling between adjacent ions or molecules.

Fig. 3 exhibits conversion data for the basic acetate and acetylacetonate

(4). Both of these ligands are bidentate with each molecule attaching to the iron through two oxygens. The values of B, and hence of $\Delta\overline{V}$, are significantly larger here than for the halides, and decrease measurably with increasing temperature. On the other hand, ferric oxalate and strontium ferric oxalate (4) $[Sr_3(Fe(C_2O_4)_3)_2 \cdot 2H_2O]$ also have bidentate ligands attached through oxygen, but both show an increase of $\Delta\overline{V}$ with temperature (Table 1). It is known that the oxalates reduce photochemically at 1 atmosphere (11, 12) and undergo a series of reactions when

Table 1. Constants A and B for the relationship $K = AP^B$.

Material	Temperature (°K)	A	B
FeCl₃	295	0.265	0.564
FeBr₃	295	0.076	0.426
KFeCl₄	295	0.091	0.497
FePO₄	295	0.079	0.457
Fe Citrate	295	0.112	0.350
K₃Fe(CN)₆	295	0.109	2.06
Fe acetylacetonate	295	1.2×10^{-5}	2.23
Fe acetylacetonate	375	0.96×10^{-2}	1.01
Fe basic acetate	378	0.22×10^{-6}	3.05
Fe basic acetate	418	2.21×10^{-2}	0.98
Fe oxalate	295	0.041	0.51
Fe oxalate	335	0.029	0.83
Fe oxalate	383	0.043	1.146
Strontium Fe oxalate	295	0.115	0.301
Strontium Fe oxalate	383	0.058	0.844
FeCl₃ · 6H₂O	294	0.063	0.95
FeF₃ · 3H₂O	294	0.027	0.95
FeF₃ · 3H₂O plus excess H₂O	294	0.072	0.95
FeCl₃ · 6NH₃ < 25 kbar	294	2.4×10^{-6}	4.06
FeCl₃ · 6NH₃ > 25 kbar	294	0.46	0.27
Fe(NCS)₃ · 6H₂O	295	0.136	0.528
K₃Fe(NCS)₆	295	0.024	0.692
Hemin	294	5.5×10^{-2}	1.53
Hemin	335	4.2×10^{-4}	2.04
Hemin	367	3.5×10^{-5}	2.57
Hematin	294	2.7×10^{-5}	2.67
Hematin	343	1.4×10^{-7}	3.77

Table 2. Heats of reaction.

Material	Pressure (kbar)	Temperature (°K)	ΔH(eV)
FeCl₃	*	323	0.12
FeCl₃	*	393	0.18
FeBr₃	*	323	0.20
FeBr₃	*	393	0.32
KFeCl₄	*	323 – 393	0.07
Fe acetylacetonate	60	325	0.15
Fe acetylacetonate	60	375	0.25
Fe acetylacetonate	150	325	0.065
Fe acetylacetonate	150	375	0.085
Fe basic acetate	75	398	0.93
Fe basic acetate	150	398	0.44
Fe oxalate	25	315	0.19
Fe oxalate	25	360	0.34
Fe oxalate	100	315	0.26
Fe oxalate	100	360	0.42
Strontium Fe oxalate	20	333	0.11
Strontium Fe oxalate	200	333	0.24
Hemin	20	335	— 0.22
Hemin	60	335	— 0.11
Hemin	90	335	— 0.057
Hematin	40	320	— 0.23
Hematin	90	320	— 0.052

* Independent of pressure